

PROJECT ADMINISTRATION DATA SHEET

☒ ORIGINAL ☐ REVISION NO. _____

Project No. A-3118

DATE 12/11/81

Project Director: Dr. A. R. Ravishankava School/Lab EML/MSB

Sponsor: Chemical Manufacturers Assn.; Washington, D.C.

Type Agreement: Agreement # FC-81-368

Award Period: From 11/9/81 To 11/8/82 (Performance) 2/8/83 (Reports)

Sponsor Amount: \$62,389 31/83 Contracted through:

Cost Sharing: none GTRI/GHP

Title: Laboratory Studies of Stratospheric Reactions

ADMINISTRATIVE DATA

OCA Contact Linda H. Bowman x4820

1) Sponsor Technical Contact:

Dr. Joseph M. Steed

CMA

2501 M. Street, N.W.

Washington, D. C. 20037

202-887-1100

2) Sponsor Admin/Contractual Matters:

Mr. John C. VanHorn

CMA

2501 M. Street, N.W.

Washington, D. C. 20037

202-887-1100

Defense Priority Rating: _____

Security Classification: _____

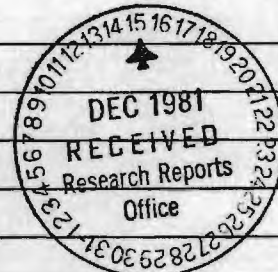
RESTRICTIONS

See Attached N/A Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval — Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of \$500 or 125% of approved proposal budget category.

Equipment: Title vests with None

COMMENTS:



COPIES TO:

Administrative Coordinator
Research Property Management
Accounting
Procurement/EES Supply Services
FORM OCA 4:781

Research Security Services
Reports Coordinator (OCA) ✓
Legal Services (OCA)
Library

EES Public Relations (2)
Computer Input
Project File
Other _____

SPONSORED PROJECT TERMINATION SHEETDate 3/22/83Project Title: Laboratory Studies of Stratospheric ReactionsProject No: A-3118Project Director: Dr. A. R. RavishankaraSponsor: Chemical Manufacturers Assn.Effective Termination Date: 1/31/83Clearance of Accounting Charges: 2/8/83

Grant/Contract Closeout Actions Remaining:

- ☒ Final Invoice and Closing Documents
☐ Final Fiscal Report
☐ Final Report of Inventions
☐ Govt. Property Inventory & Related Certificate
☐ Classified Material Certificate
☐ Other _____

Assigned to: EML (~~School~~/Laboratory)COPIES TO:

Administrative Coordinator
Research Property Management
Accounting
Procurement/EES Supply Services

Research Security Services
Reports Coordinator (OCA)
Legal Services (OCA)
Library

EES Public Relations (2)
Computer Input
Project File
Other

First Quarterly Report

LABORATORY STUDIES OF STRATOSPHERIC REACTIONS

Performance Period November 9, 1981 through January 31, 1982

A-3118

February 8, 1982

During the first quarter of this program the apparatus needed to carry out many of the proposed studies is being constructed. The Ar^+ laser and the dye laser are operational and ready for use. The long path laser absorption system is also ready for use.

The initial experiments to be carried out involve photolysis of chlorine nitrate. The primary aim is to find out if chlorine nitrate could be a good photolytic source for NO_3 free radicals. However, since it is needed for stratospheric modeling calculations, the quantum yields for NO_3 , $\text{O}(^3\text{P})$ and $\text{Cl}(^2\text{P})$ in chlorine nitrate photolysis will be measured.

A-3/18

2nd QUATERLY PROGRESS REPORT ON CMA PROJECT:
"Laboratory Studies of Stratospheric Reactions"

CONTRACT # FC 81-368
Ga. Tech Project # A-3118

The apparatus to be used for carrying out NO_3 photochemistry and kinetics studies is now completely assembled and is operational. This apparatus is described below.

A schematic diagram of the apparatus is shown in the attached figure. A 25 cm long, 2" i.d. glass reaction cell with six ports in the middle is used. The geometry of the ports is shown in the figure. The white cell mirrors are 2" in diameter and have radii of curvature of 0.5 m. One of the mirrors was cut in half to provide a matched set of half circles. The mirrors are dielectric coated for greater than 99.7% reflection in the red. The mirrors are arranged as shown in the figure. The probing laser beam from the dye laser enters through the slit between the split mirrors, makes a variable number of passes and exists close to the incoming beam. A fraction of the input beam is split and measured by a photodiode. The transmitted beam is measured by another photodiode. We have built an analog divider which takes the ratio of the intensities of the two beams and amplifies it by a factor of 10. Using the white cell arrangement we can make up to 100 passes. This upper limit arises because the incident and the transmitted beams are totally superimposed if more passes are made. Windows W1 and W2 are Ar coated so that there are not reflective losses and ghost beams. Since the analog divider takes the instantaneous ratios of the incident and transmitted light intensities, any laser fluctuations in the laser beam intensity do not effect the measured ratio of I/I_0 so that we can measure 0.1% absorption with $\sim 3\%$ accuracy. Using 100 passes (25 m path length) and 0.1% absorption, we can accurately measure $2 \times 10^{10} \text{ cm}^{-3}$ of NO_3 . The detection limit for NO_3 is of course much better.

The output of the Ar ion laser is split into two beams. 70% of the light is used to pump the dye laser (i.e. to monitor NO_3). The rest (30%) is passed through the center of the cell using ports equipped with

Brewster windows to monitor NO_2 via laser induced fluorescence. Currently, we are using all lines to pump NO_2 laser induced fluorescence. This method is adequate to monitor the NO_2 concentrations expected in the experiments to be carried out in the near future, since they will all be low pressure studies. However, we would like to separate the 488 nm beam from the 512 nm beam, use the 512 nm beam to pump the dye laser and the 488 nm beam for NO_2 laser induced fluorescence detection. This modification will improve the NO_2 detection and will enable us to detect low concentrations even at higher pressures.

The oxygen atom detection via resonance fluorescence is currently not incorporated into the system. However, it can be installed very easily at any given time.

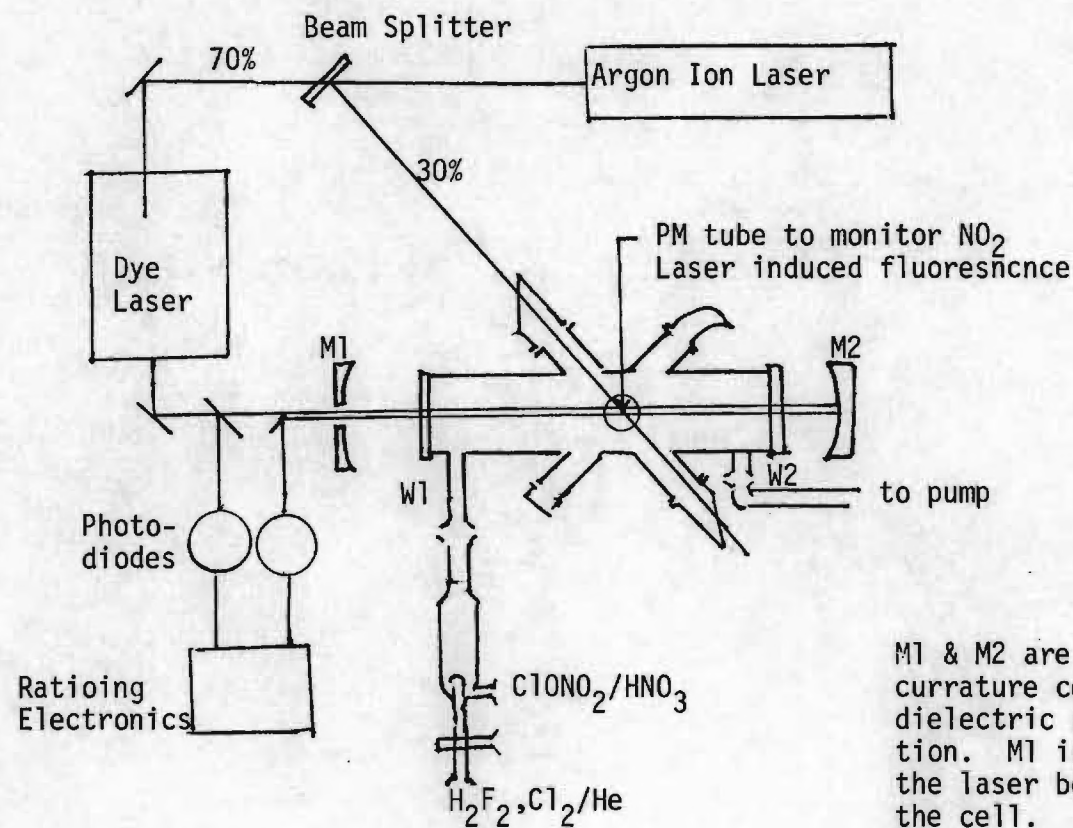
The flow tube and the associated gas handling and metering system is completely assembled. The inside of the flow tube is coated with halocarbon wax. Currently, we have a glass and a quartz microwave discharge tubes. In the near future they will be replaced by an alumina tubing so that F_2 can be discharged without the simultaneous generation of oxygen atoms.

Work to be carried out during the next quarter:

(1) J. Margitan (at JPL) has already measured the quantum yields for the production of Cl and O atoms in the photolysis of ClONO_2 and found Cl to be major product. Therefore we will not repeat those experiments. We will only measure the quantum yield for NO_3 production. Also, Margitan has measured the rate coefficient for $\text{Cl} + \text{ClONO}_2$ reaction to be $\sim 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ much faster than currently believed. Therefore, it is necessary to identify the products of this reaction. We will measure the yield of NO_3 from this reaction by monitoring NO_3 while adding Cl atoms to ClONO_2 in the flow tube. It is suspected that NO_3 is the major product of this reaction.

(2) Using $\text{Cl} + \text{ClONO}_2$, $\text{H} + \text{ClONO}_2$, or $\text{F} + \text{HNO}_3$ as the source of NO_3 , we will measure the absorption cross section of NO_3 at a few selected wavelengths between 560 and 665 nm. In these experiments, NO_3 concentration will be measured by titrating it with NO. If the measured cross sections

agree with published results . The cross section measurement task will be stopped. Otherwise, we will measure the cross section over a wide range of wavelengths.



M1 & M2 are a matched pair of 0.5 m curvature concave mirrors which are dielectric coated for $> 99.7\%$ reflection. M1 is cut in half to allow the laser beam to enter and leave the cell.
 W1 & W2 are 1/2" thick quartz windows which are AR coated on both sides.

Third Quarterly Progress Report on CMA Project:
"Laboratory Studies of Stratospheric Reactions"

Contract #FC 81-368
Georgia Tech Project #A-3118

Since submitting the previous progress report we have purchased two photoamp photodiode systems which have built-in preamp and amplifiers whose gains are well matched. Using these photodiodes in conjunction with the analog divider, compensation for the fluctuations in the laser intensities can be very easily carried out and this improves our NO_3 detection capability. We have also recently obtained ClF_3 and we are in the process of synthesizing ClF which is a starting material for ClONO_2 synthesis (no Cl_2O is formed in this method).

The major reason for the lack of expected progress in this quarter is the absence of one of the principal investigators (ARR) for 45 days during the summer (attending meetings in Israel and Germany plus vacations!) in addition to other personnel being on vacation. The good news is now we can concentrate on the CMA project during this quarter.

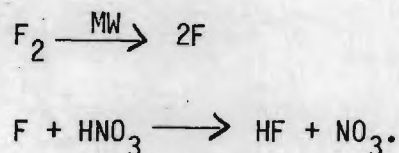
At the present time, it seems quite clear that the project cannot be completed in the allotted time. Therefore, within the next two months we will need to request a no-cost extension on this project. However, we would like to carry out some of the preliminary experiments, to get a better idea of how much more time it would take, before requesting such an extension.

QUARTERLY PROGRESS REPORT ON CMA PROJECT:

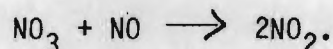
"Laboratory Studies of Stratospheric Reactions"

CMA CONTRACT # F81-368
Ga. Tech Project # A-3138

We have just finished measuring the absorption cross-section of NO_3 free radical in the wavelength region of 570 to 730 nm region. NO_3 free radicals were produced by the reaction of F atoms (produced by microwave discharge of F_2/He mixture) with HNO_3 .



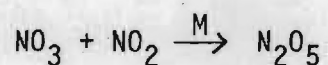
The absolute concentration of NO_3 was determined by titrating it with NO using the fast reaction,



NO_3 concentration ranged from 1 to $3 \times 10^{13} \text{ cm}^{-3}$. The region of 600 to 730 nm was covered using DCM dye in the ring dye laser and the region of 570-640 nm was covered using the Rhodamine 6G dye. The optical path length was between 650 and 895.4 cm (cell length 40.7 cm) so that the percentage of absorption ranged from 50 to 0.1%. The precision of the measurement ranged from 0.5 to 3%.

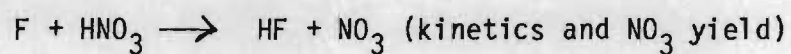
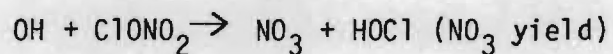
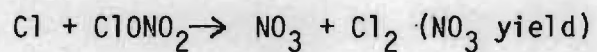
The measured absorption cross section at 298K is shown in Figure 1. In addition, the cross sections at the individual argon ion laser lines were also measured. They are shown in table 1.

Preliminary kinetic studies on the following reactions have also been carried out:



Upon completion of the measurements the results will be reported.

Preliminary studies on the following reactions are underway:

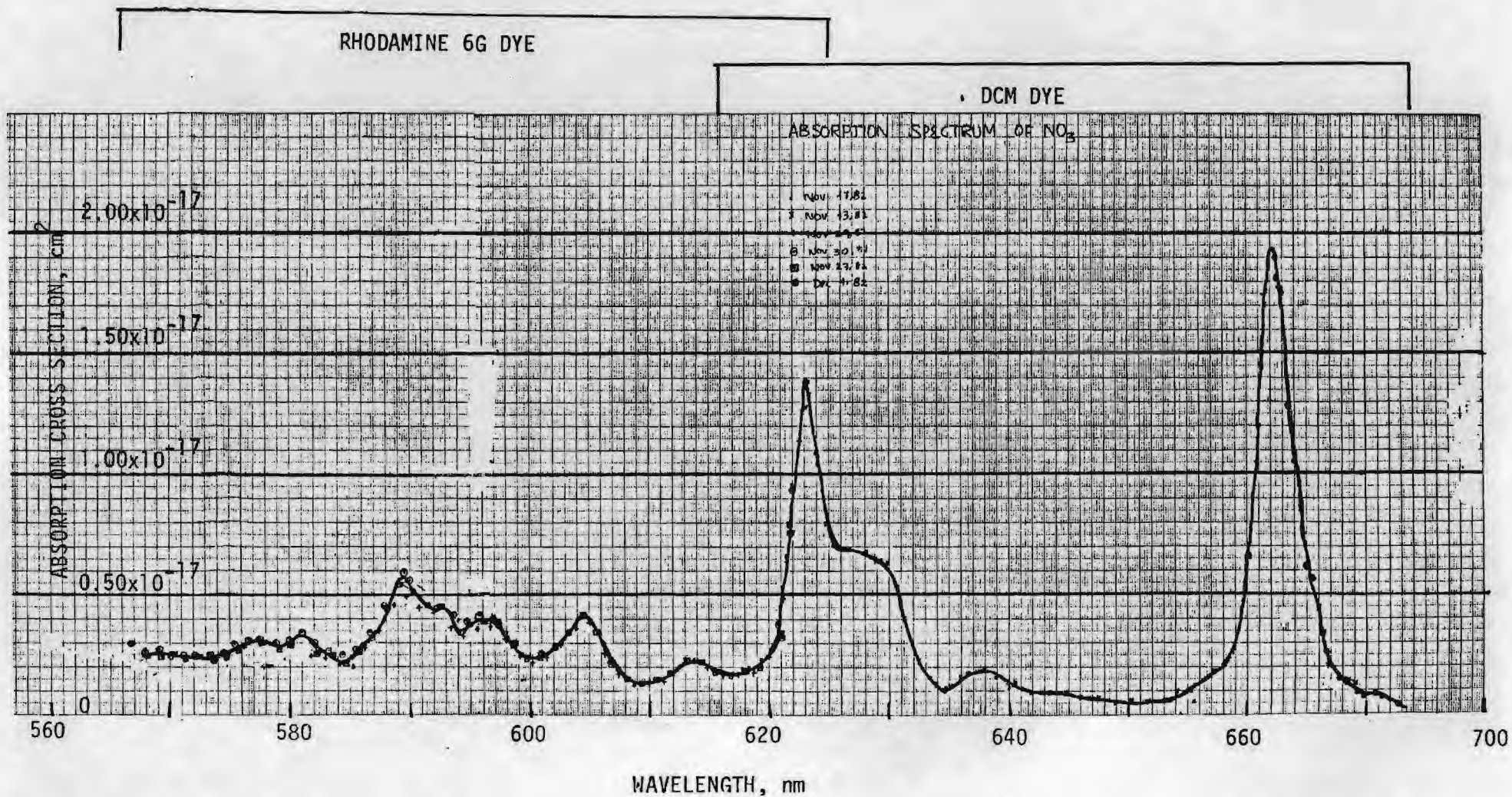


The last reaction is just to further characterize our NO_3 source.

Table 1. Absorption Cross Section of NO_3 at Ar ion Laser Lines

λ, nm	$\sigma \times 10^{20}, \text{cm}^2/\text{molecule}$
457.9	23
476.5	76
488.0	75
496.5	120
501.7	97
514.6	146

FIGURE 1
ABSORPTION SPECTRUM OF NO₃



A-3118

LABORATORY STUDIES OF STRATOSPHERIC REACTIONS:
CHEMISTRY AND PHOTOCHEMISTRY OF THE NO₃ RADICAL

by

A. R. Ravishankara

P. H. Wine

Prepared for:

Chemical Manufacturers Association

Contract No. 81-368

Georgia Institute of Technology

Engineering Experiment Station

Atlanta, Georgia 30332

TABLE OF CONTENTS

	<u>Page No.</u>
Abstract	1
NO ₃ Absorption Cross-Section Measurements	3
NO ₃ + NO ₂ Reaction	11
Laser Induced Fluorescence from NO ₃	12
NO ₃ + CO Reaction	16

ABSTRACT

A one year research program has been carried out with the goal of better defining the atmospheric chemistry of the NO_3 radical. The following experimental work was performed:

- (1) A discharge flow-long path absorption system was constructed and used to measure absolute absorption cross sections for NO_3 over the wavelength range 458-672 nm at 298 K. NO_3 was produced cleanly by the reaction $\text{F} + \text{HNO}_3 \rightarrow \text{HF} + \text{NO}_3$ and the NO_3 concentration was determined via the titration reaction $\text{NO}_3 + \text{NO} \rightarrow 2\text{NO}_2$.
- (2) The discharge flow-long path absorption apparatus was modified such that 120 passes through a 1 cm^2 (perpendicular to the flow) region of a 4.5 cm absorption cell were achieved, thus allowing long path absorption detection to be employed to monitor NO_3 in kinetics studies. Preliminary studies of the reaction $\text{NO}_3 + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M}$ have been carried out.
- (3) Laser induced fluorescence from NO_3 has been detected. The detection sensitivity obtained is about three orders of magnitude better than that obtained by long path absorption, thus allowing very fast reactions of NO_3 to be studied. A detailed study of the reaction $\text{NO}_3 + \text{NO} \rightarrow 2\text{NO}_2$ has been initiated.

Abstract (continued)

- (4) The reaction $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$ was investigated using long path absorption detection of NO_3 . No reaction was observed, thus allowing an upper limit of $1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to be placed on the rate constant for this reaction at 298K.

FINAL TECHNICAL REPORT

Project A-3118

NO₃ Absorption Cross Section Measurements

The absorption cross section measurements were carried out in a specially designed discharge flow apparatus. A schematic diagram of this apparatus is shown in Figure 1. The apparatus consisted of three sections: (a) a conventional discharge flow tube where NO₃ could be prepared and titrated with NO, (b) a laser induced fluorescence detection cell used to monitor NO₂ and (c) an absorption cell to measure the NO₃ absorption cross section. The halocarbon wax coated discharge flow tube was equipped with either an uncoated pyrex or a ceramic discharge tube where an F₂/He mixture was subjected to the microwave discharge. The effluents from the discharge flowed into a stream of He which was introduced upstream of all gases. HNO₃ was introduced approximately 2 cm downstream of the F atom entrance. NO₃ produced by the reaction of F with HNO₃ flowed down the discharge tube and entered a 1 cm id fluorescence cell. The fluorescence cell was equipped with two ports through which ~ 150 mW of Argon ion laser beam was transmitted. At right angles to the excitation beam, the fluorescence (from NO₂) was collected by a lens, passed through a set of filters to remove scattered laser radiation and detected by a PM tube. The amplified PM tube output was fed to a counter. The absorption cell was attached to the fluorescence cell. The gas mixture was pumped out after flowing through the absorption cell. The absorption cell was equipped with anti-reflection coated 1/2" thick windows. The cell was located between mirrors in a white cell arrangement. The mirrors were dielectric coated to reflect greater than 99.9% over the entire visible wavelength region. The probing light beam was multipassed through the cell between 14 and 20 times to obtain a path length of 560 to 800 cm.

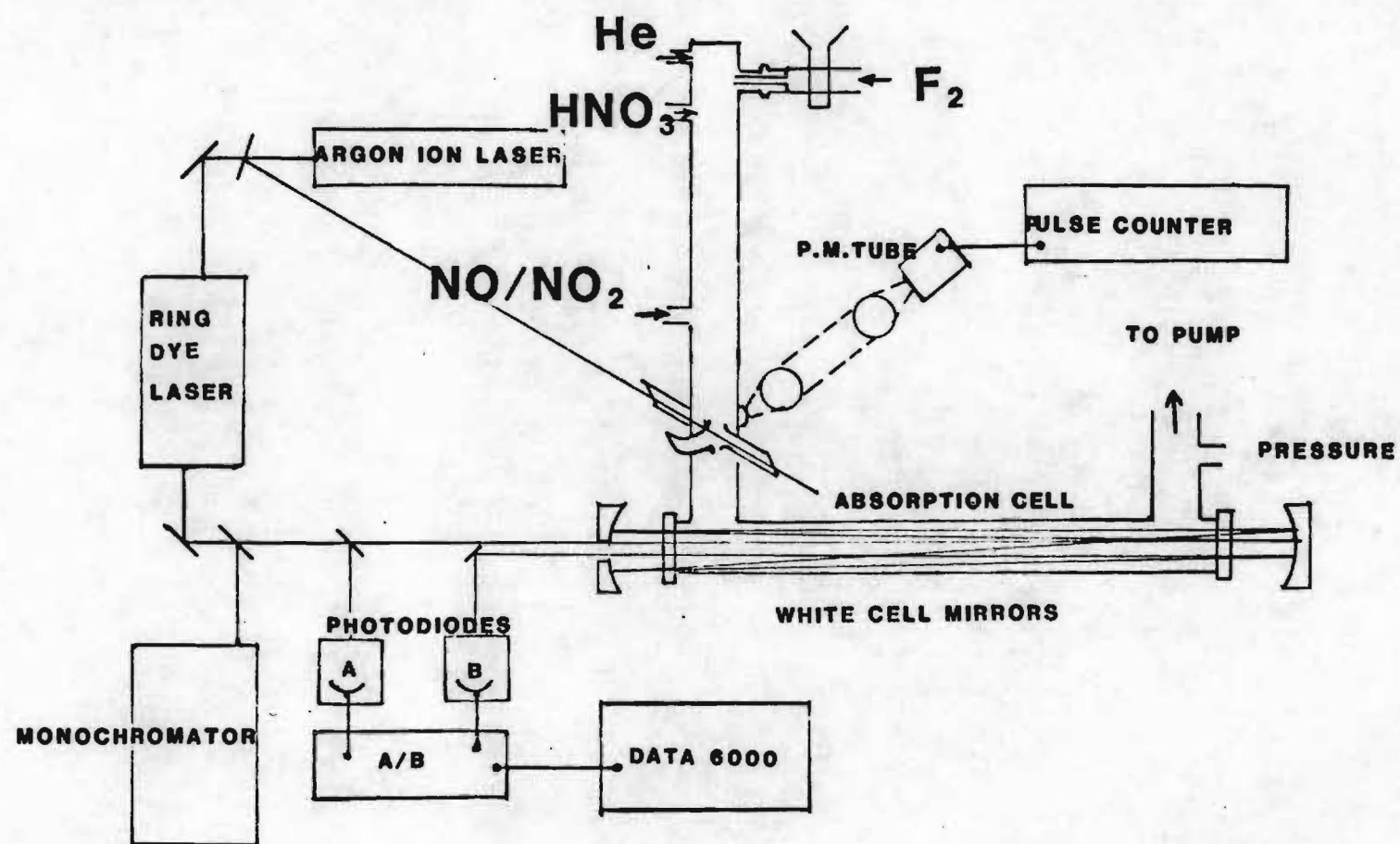
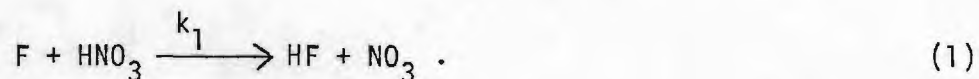


Figure 1. Schematic of the apparatus for absorption cross-section measurements.

NO_3 was produced by the reaction of F atoms with HNO_3 ,



F atoms were produced by the microwave discharge of a mixture of F_2 in He in an uncoated pyrex tube or an alumina tube. [we found the uncoated pyrex tube to be just as good as the alumina tube]. By keeping the microwave power very low ($\sim 5\text{w}$) we could obtain nearly complete dissociation of F_2 . NO_3 loss was found to be negligibly slow in the flow tube once it was coated with halocarbon wax.

The probing laser beam was generated by pumping a tunable ring dye laser with all lines of an Argon ion laser. During the course of this work two different dyes were used in the dye laser. For the wavelength region 613 to 683 nm, DCM dye was used while Rhodamine 6G was used to cover the wavelength range 565 to 625 nm. (Thus there was a region of wavelength overlap). The wavelength of the probing beam was measured by diverting a small fraction of the beam onto a 3/4 meter Spex monochromator calibrated using He-Ne, and Argon ion laser lines. The absolute accuracy of wavelength is estimated to be better than 0.05 nm. The line width of the dye laser output was measured using an etalon assembly and found to be 0.002 nm. A fraction of the beam going into the absorption cell was picked off by a quartz plate and measured by photodiode A. The transmitted beam was taken out of the white cell after it had been multipassed a known number of times and measured by photodiode B. An analog divider took the ratio of the outputs from photodiodes A and B (response time 100 KHz) and the output of the divider was sampled every 20 μsec by a signal analyzer. The averaging period varied from 10 to 1000 sec. The precision of the transmitted light intensity normalized to any fluctuations in laser power depended on the averaging period and for 10 second integration time it was typically $5 \times 10^{-2}\%$!

With the above arrangement, we could monitor changes in transmitted light intensities of $\sim 0.05\%$ easily. In addition, we could simultaneously measure the concentration of NO_2 in the flow tube using LIF. A port located ~ 5 cm above the fluorescence cell was used for adding NO into the flow.

NO_3 Concentration Measurement: The concentration of NO_3 in the flow tube was determined by titrating it with NO. To monitor the titration, two different approaches were used: (a) Monitor the absorption of NO_3 and (b) Monitor NO_2 concentration via laser induced fluorescence. Results of one titration experiment where both $[\text{NO}_3]$ and $[\text{NO}_2]$ was monitored is shown in Figure 2. As the amount of added NO is increased, the absorbance goes down indicating the removal of NO_3 and concurrently the $[\text{NO}_2]$ goes up. As can be seen in Figure 2, the endpoint of the titration can be easily located. Three points are to be noted: (a) There is a finite concentration of NO_2 even in the absence of added NO. (will be discussed later), (b) The absolute concentration of NO_2 produced upon addition of NO is measured since the laser induced fluorescence of NO_2 is calibrated and (c) for each NO_3 removed 2 molecules of NO_2 are formed. The concentration of NO added was calculated based on measured mass flow rates and the pressure in the system. NO was drawn from a bulb containing NO and He, and the concentration of NO in this bulb was measured by converting NO to NO_2 (by addition of oxygen) and measuring NO_2 concentration by UV absorption.

Characterization of NO_3 Source: In order to ensure that there were no other absorbing species in our NO_3 source a number of experiments aimed at elucidating the chemistry in the source were carried out. It was noticed that we could not titrate HNO_3 with F atoms, i.e. $[\text{NO}_3]$ formed did not increase linearly with $[\text{HNO}_3]$. It was apparent that F atoms were removing NO_3 unless all F atoms were quickly converted to NO_3 . Based on this behavior the rate coefficient for $\text{F} + \text{NO}_3$ was

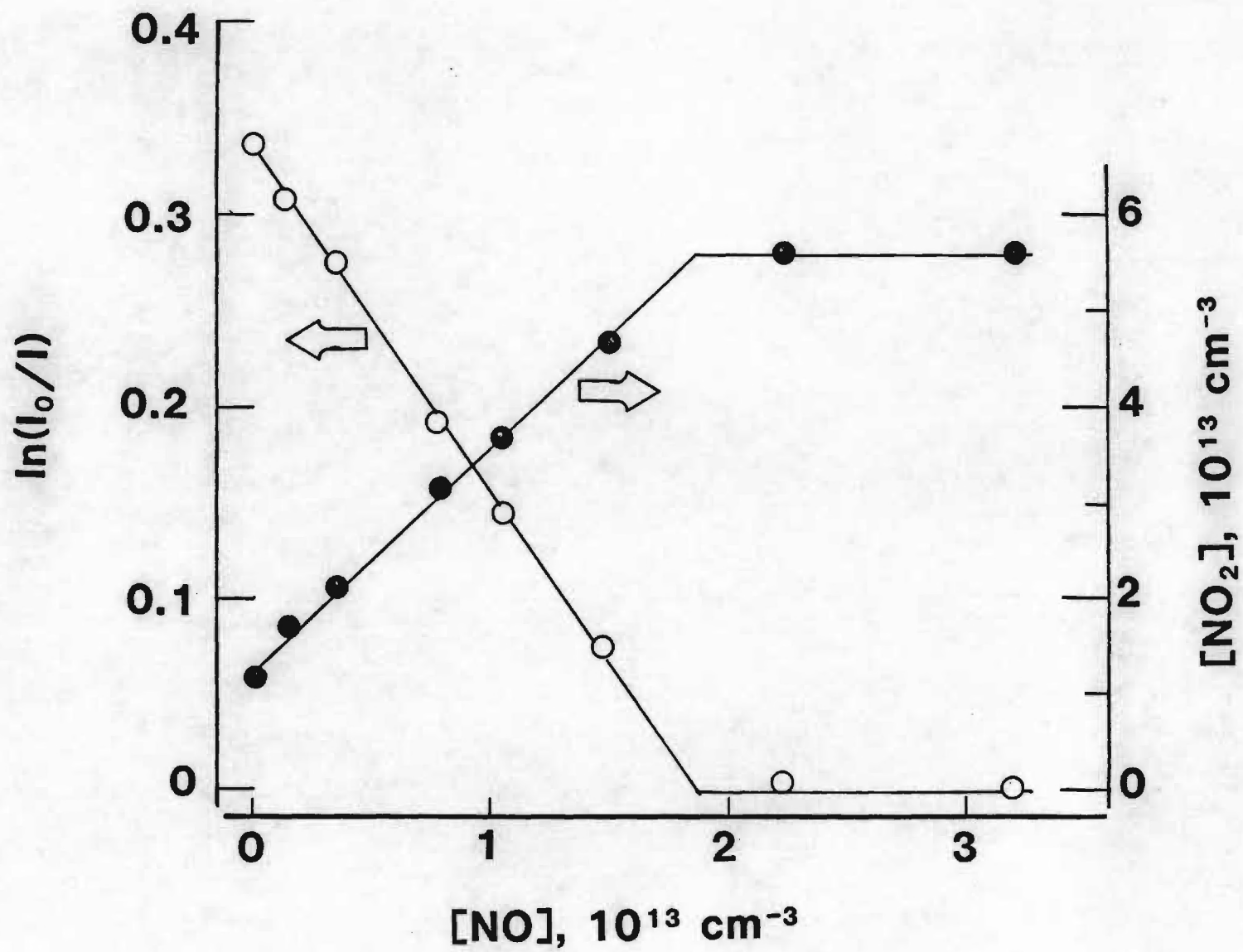
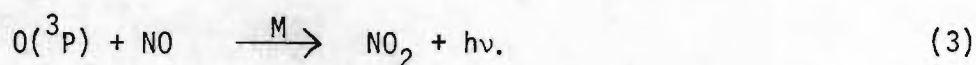


Figure 2. Typical NO_3 titration experiment.

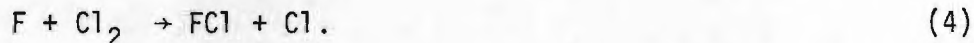
deduced to be very rapid i.e., $> 5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. It is well known that F_2 discharges produce O atoms. It was suspected that the NO_2 produced in the source was due to the reaction of O with NO_3 ,



This suspicion was confirmed by monitoring $\text{O}(^3\text{P})$ via the chemiluminescent reaction,



As mentioned earlier, it was not possible to titrate F atoms with HNO_3 . Therefore, to determine the yield of NO_3 in reaction (1), we measured the absolute concentration of F atoms produced by titrating with Cl_2 ,



The Cl atom concentration was followed by the chemiluminescent recombination reaction,



To the known concentration of F atoms excess HNO_3 was added and the concentration of NO_3 produced was measured by absorption as well as by converting it to NO_2 (by addition of NO) and measuring NO_2 . After accounting for reaction (2), it was determined that the yield of NO_3 in reaction (1) is unity.

We are confident that our source of NO_3 is very clean and produces NO_3 with a small amount of NO_2 .

Determination of NO_3 Cross Section: In experiments where the NO_3 absorption cross section was measured, $\sim 1 \times 10^{13} \text{ cm}^{-3}$ of NO_3 was produced. After running NO_3 through the flow tube for approximately 15 mins, the concentration of NO_3 was determined by titration. (At all times, the concentration of added HNO_3 was at least 5 times larger than that of F atoms.) The titrations were carried out by monitoring the NO_3 concentration by absorption at either the peaks of the 662 nm band or the 623 nm band. At the same time, $[\text{NO}_2]$ was also monitored. Upon completion of the titration, the wavelength was changed to the desired wavelength and I , the transmitted laser beam intensity with NO_3 present, was measured. I_0 , the intensity of the transmitted laser beam with no NO_3 , was determined in two ways: (a) HNO_3 was turned off so that NO_3 was not produced and (b) excess NO was added above the fluorescence port to convert all NO_3 to NO_2 . The agreement between these two methods was excellent at wavelengths greater than 565 nm, thus showing that no other species was contributing to the measured absorption. This is particularly important since $[\text{NO}_2]$ was too small to be affecting our measurements. Measurement of I_0 at each wavelength was necessary because small changes in the transmission characteristics of the absorption cell windows and in the reflectivity of white cell mirrors are amplified because of multipassing the beam. After carrying out measurements over the entire range of wavelengths that could be obtained by using a particular dye in the dye laser, the wavelength was changed back to the peak of the absorptions and the $[\text{NO}_3]$ redetermined. Since our laser is not equipped with a continuously tunable birefringent filter, measurements were made at distinct wavelengths. To cover the entire range of 565 to 673 nm, two different dyes were used. Six separate scans were carried out and the average of these scans is shown in Figure 3.

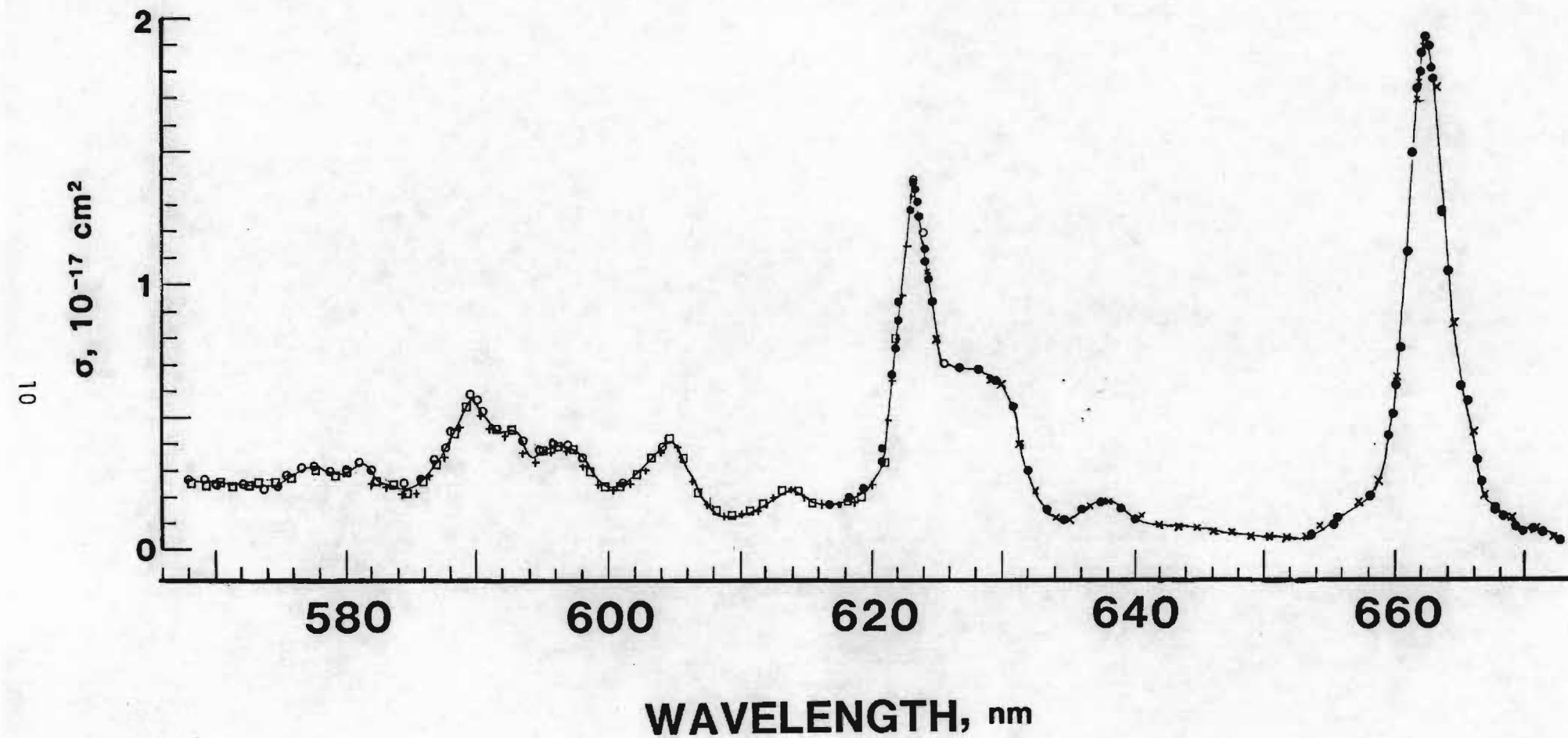


Figure 3. NO_3 absorption spectrum.

In addition to these measurements, absorption cross sections for NO_3 at individual argon ion laser line wavelengths were also measured. The measured values are not as accurate ($< 20\%$) as those shown in Figure (3) for two reasons: (a) The laser had to be realigned after carrying out the titrations and hence it is possible that the NO_3 concentration could have changed slightly during this period, and (b) Contributions due to absorption by NO_2 had to be subtracted. The measured cross sections are shown in Table 1.

$\text{NO}_3 + \text{NO}_2$ Reaction:

The study of this reaction has not been completed but will be completed in the near future. The apparatus used for this study differs from that used for the absorption cross section measurements in one important way--the single pass path length of the absorption cell is only 4.5 cm, but the net path length remains long (~ 560 cm). The long path length is obtained by multipassing the beam over 120 times through a very small area (~ 1 cm x 1 cm), a feat which is made possible by placing the absorption cell at the focus of the white cell arrangement. The reason for using a very small sampling volume is that no corrections need to be made for the time it takes for NO_3 to flow through the detection volume--it is essentially instantaneous. The discharge tube is the same as that used in cross section measurements described earlier except that a sliding injector is added.

As before, NO_3 is made by the reaction of F with HNO_3 . NO_2 is added through the injector and the concentration of NO_3 is monitored as a function of NO_2 concentration and the distance between the injector tip and the detection zone. The NO_2 concentration is maintained much higher than that of NO_3 and the reaction is studied under pseudo first order conditions in NO_3 . Figure 4 shows plots of the change in NO_3 concentration as a function of NO_2 at fixed

reaction distance and a fixed system pressure. By varying the reaction distance different curves are obtained from which the rate coefficients can be calculated. Since all our experiments are not completed we do not wish to present any numbers at this time. It should be noted, of course, that this rate coefficient has to be measured as a function of system pressure as well as the identity of the diluent gas.

Laser Induced Fluorescence from NO_3 :

We have detected laser induced fluorescence from NO_3 . [Two other groups have previously reported observing LIF; McDonald's group at NRL and Tanaka's group in Japan]. A pulsed Nd:Yag laser pumped tunable dye laser was used for these experiments. Using DCM dye we scanned a wavelength range of 620 to 680 nm. NO_3 was produced, as before, by the $\text{F} + \text{HNO}_3$ reaction. The fluorescence was viewed through a filter which cut off at 690 nm by a Hamamatsu red sensitive PM tube. The excitation spectrum (not normalized for detection system response factor) is shown in Figure 5. The fluorescence is quite strong. We are currently making system modifications to maximize the detection sensitivity using this method. The lifetime of excited NO_3 was also measured; however, it was dominated by quenching as indicated by its variations with pressure.

The main aim of this work was to develop another sensitive NO_3 detection method. We are planning on using this system to carryout many NO_3 kinetic studies such as the reactions of NO_3 with NO , and $\text{O}(^3\text{P})$ and, in fact, work on the $\text{NO}_3 + \text{NO}$ reaction has begun. We estimate that $\sim 10^9 \text{ cm}^{-3}$ of NO_3 can be readily detected by LIF.

Table I. Absorption Cross Sections for NO_3 at Wavelengths of Several Argon Ion Laser Lines

$\lambda(\text{nm})$	$10^{20} \sigma (\text{cm}^2)$
457.9	23
476.5	76
488.0	75
496.5	120
501.7	97
514.6	146

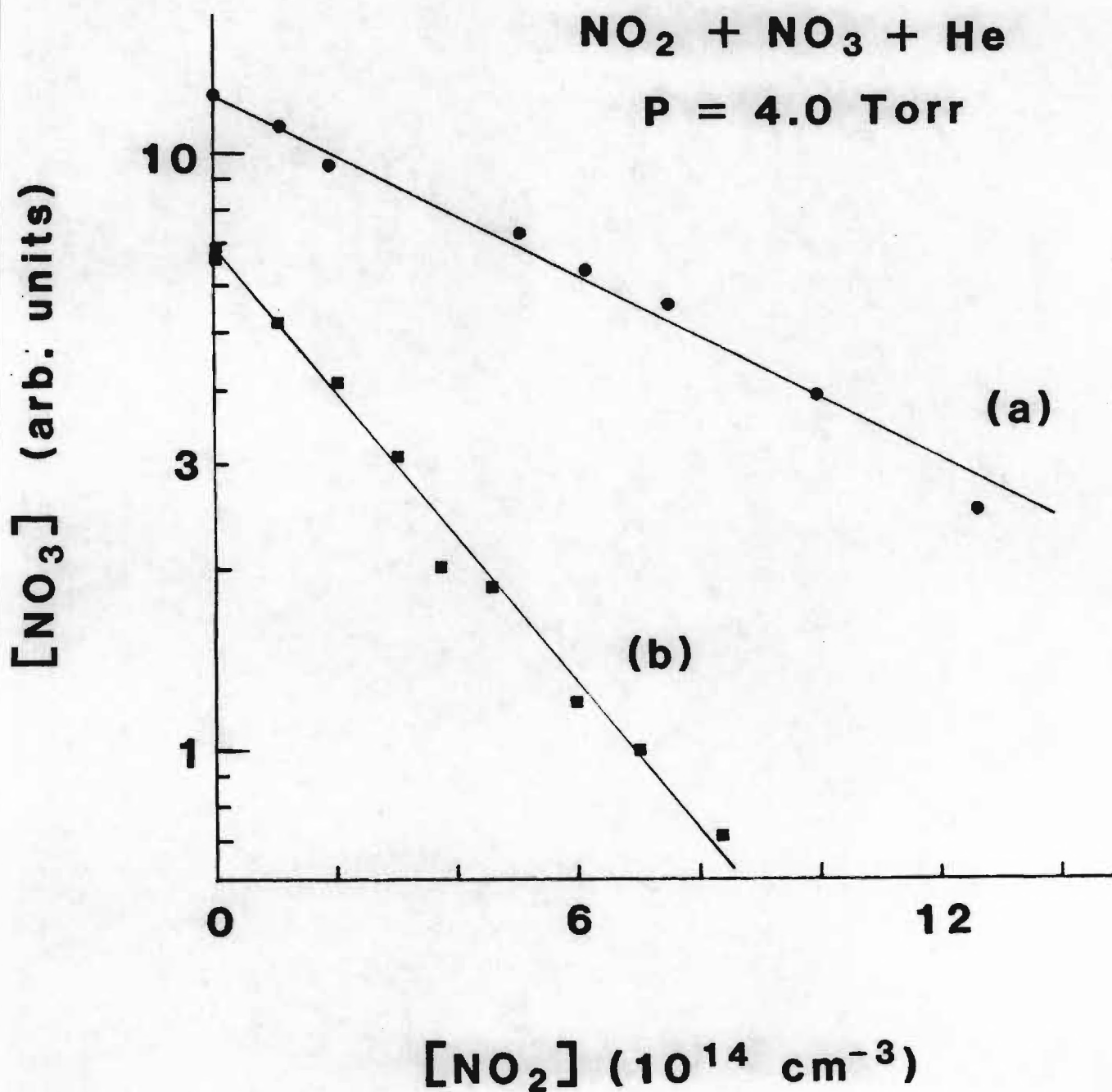


Figure 4. Typical data for the reaction of $\text{NO}_2 + \text{NO}_3 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M}$. The distance from the tip of the injector to the center of the absorption cell was 7.9 cm in (a) and 16.1 cm in (b).

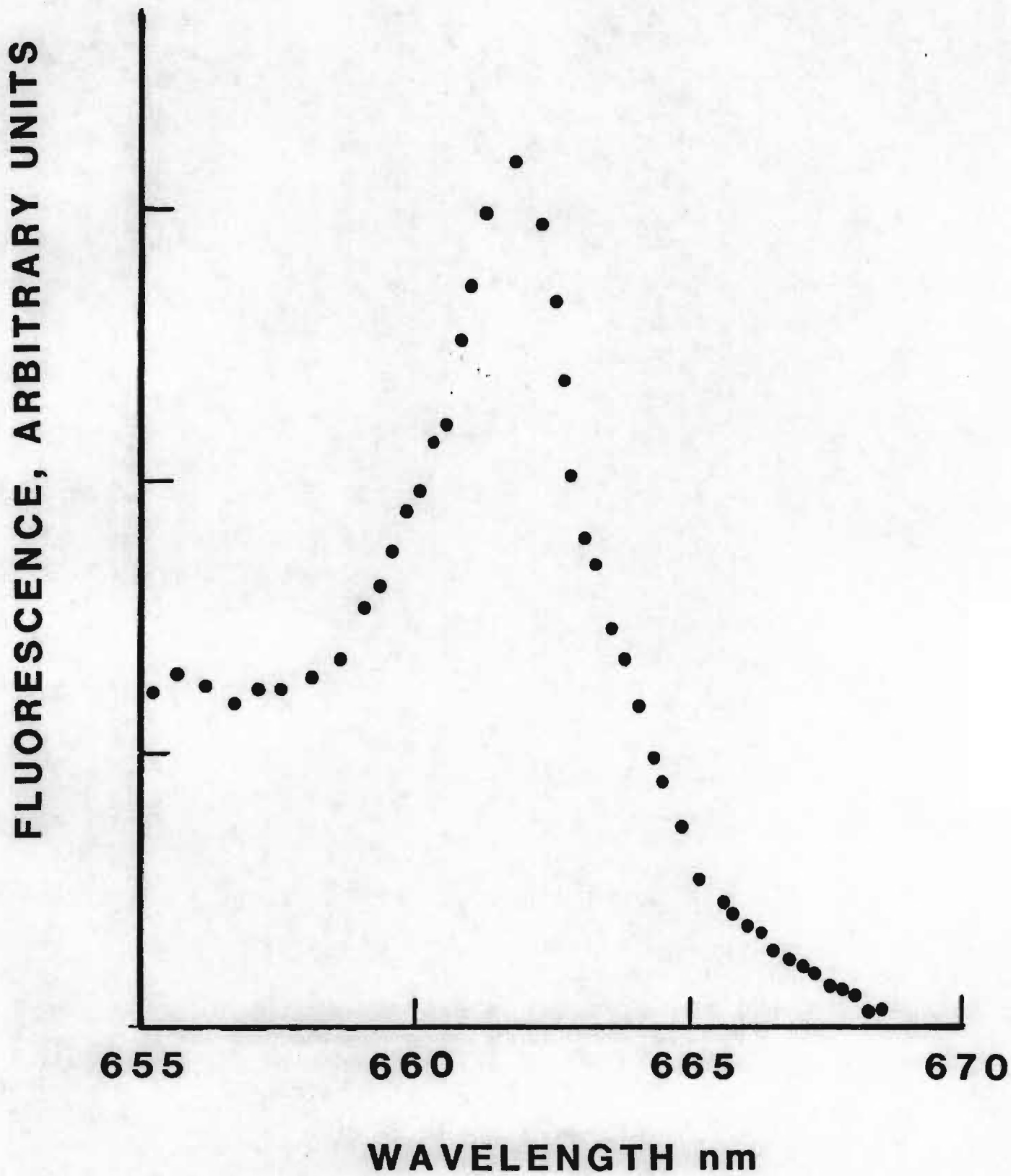


Figure 5. NO_3 fluorescence excitation spectrum.

NO₃ + CO Reaction:

Some preliminary experiments were carried out to investigate the possibility that NO₃ would react with CO. [It is worth pointing out that the temporal behavior of NO₃ in the stratosphere points towards a missing reaction, most likely with a stable molecule]. Large concentrations of CO were added to the flow tube at a point where the NO₃ generation reaction had gone to completion. The reaction is very slow and we could only place an upper limit of $1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ on the rate constant for this reaction.